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B. Little, J. Lee, R. Ray

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Both microfouling (biofilms) and macrofouling can influence corrosion in marine environments. Biofilms force an increase in open circuit potential (ennoblement) for passive alloys and an increase in cathodic kinetics. The result is a decrease in initiation time for crevice corrosion for some stainless steels and increase propagation rate for galvanic corrosion for some couple metals. A specific type of carbon sheet piling corrosion, accelerated low water corrosion,k has been attributed to a microbiologically generated sulfur cycle in the presence of heave macrofouling in tidal zones. Ennoblement and carbon steel sheet piling corrosion have been observed in fresh water, but the mechanisms producing these two phenomena are specific to the environments.

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marine corrosion, ennoblement, accelerated low water corrosion, stainless steel, carbon steel

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HOW MARINE CONDITIONS AFFECT SEVERITY OF MIC OF STEELS

B. LITTLE, J. LEE & R. RAY
Naval Research Laboratory
Stennis Space Center, MS 39529-5004

SUMMARY: Both microfouling (biofilms) and macrofouling can influence corrosion in marine environments. Biofilms force an increase in open circuit potential (ennoblement) for passive alloys and an increase in cathodic kinetics. The result is a decrease in initiation time for crevice corrosion for some stainless steels and increased propagation rate for galvanic corrosion for some coupled metals. A specific type of carbon sheet piling corrosion, accelerated low water corrosion, has been attributed to a microbiologically generated sulfur cycle in the presence of heavy macrofouling in tidal zones. Ennoblement and carbon steel sheet piling corrosion have been observed in fresh water, but the mechanisms producing these two phenomena are specific to the environments.

Keywords: marine corrosion, ennoblement, accelerated low water corrosion, stainless steel, carbon steel

INTRODUCTION: Exposure of any engineering material to naturally occurring seawater initiates a series of sequential and parallel biological and chemical events that culminate in the formation of a complex layer of inorganic, organic, and cellular components known as biofouling. Biofouling is a general term used to describe both the microbiological and macrobiological growths that develop on exposed surfaces. Gubner and Beech[1] evaluated the parameters that affect the corrosivity of natural seawater (Table 1) and concluded that the general microbial population, in addition to specific types of marine microorganisms, i.e., sulfate reducing (SRB), sulfur-oxidizing bacteria (SOB) and chemo-organotrophic bacteria,

Table 1
Parameters That Can Affect The Corrosivity Of Seawater[1]

- Biochemical oxygen demand
- Chemical oxygen demand
- Total organic carbon
- Total aromatic compounds
- Polycyclic aromatic hydrocarbons
- Inorganic compounds, (i.e. PO_4^{2-}, NO_3^-, SO_4^{2-}, S^{2-}, CN, NH_4^+)
- Heavy metal ions, (i.e. Fe, Cr, Cu, Ni, Hg, Zn, Sn)
- Bacteriological analysis
  - Most Probable Number (MPN) for sulfate-reducing bacteria
  - MPN for sulfur-oxidizing bacteria
  - MPN for chemo-organotrophic bacteria
  - Total bacterial count

could affect corrosivity. The influence of micro- and macrofouling on corrosion rate can range from acceleration to inhibition. The challenge from the corrosion engineering perspective is to determine when the influence of the organisms is important enough that effective corrosion control cannot be achieved without specifically addressing the microbial effect. The following sections will address two types of biofouling that produce unique consequences in marine environments.

At temperatures below 60°C resistance to crevice corrosion is the limiting factor for selecting alloys for seawater service and crevice corrosion is the most problematic issue affecting the performance of stainless steels in seawater. Several investigators[2-7] have documented the tendency for marine biofilms to cause a noble shift, or an ennoblement, in open circuit potential (OCP) of passive alloys. The alloys tested include, but are not limited to: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, platinum, gold, palladium, chromium, titanium, and nickel R50250 (Figure 1). Ennoblement of OCP has been reported in fresh, brackish and seawaters. In fresh and brackish water, ennoblement is related to microbial deposition of manganese. Ennoblement in marine waters has been ascribed to depolarization of the oxygen reduction reaction, due to organometallic catalysis, acidification of the electrode surface, the combined effects of elevated H_2O_2 and decreased pH and the production of passivating siderophores. Despite

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the extensive literature on the subject, the exact mechanism of ennoblement of metals in seawater remains unresolved.

Theoretically, potential ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation. However, attempts to relate biofilms to increased localized corrosion have been inconsistent. Dexter and co-workers[8-11] showed that the critical potential for pit initiation (E_{cpp}) on an open surface and the breakdown potential for initiation of localized corrosion (E_b) at occluded sites in seawater (salinity 26-31 ppt) or the air/water interface were affected by formation of biofilms. For alloy S30400, the average E_{cpp} with biofilms (425 ± 24 mV SCE) was 95 mV higher than that of the bare samples (330 ± 35 mV). For alloy S31600, the E_{cpp} values of the biofilmed samples (500 mV) were not much different from those of the bare samples (480 ± 17 mV). E_b for alloy S30400 increased from 60 mV for the bare sample to 260 ± 20 mV for those with biofilms. For alloy S31600 E_b increased a smaller amount from 300 mV for the bare sample to 390 ± 14 mV for those with biofilms. Tests on passive alloys S30400 and S31600 indicated that crevice initiation times were reduced when natural marine biofilms were allowed to form on the boldly exposed external cathode surface of crevice corrosion samples. Even though there was variability in the data, the authors concluded that ennoblement of OCP in the presence of natural biofilms usually caused the alloy to reach its E_b for crevice initiation faster than when the test was repeated under control conditions without the

Figure 1. Potential ennoblement in natural seawater at Futtsu City (Tokyo Bay) from Mar. 15 to Apr. 12 in 2000.[7] © NACE International 2002

biofilm. The authors concluded that ennoblement of OCP decreased the salinity level below which a given alloy should be resistant to localized corrosion initiation.

Several investigators have used potentiodynamic polarization curves to show that cathodic kinetics are increased during biofilm formation on passive alloy surfaces.[12,13] Tests have shown that this increase in kinetics results in higher propagation rates for crevice corrosion. Crevice propagation rates after initiation were significantly and consistently enhanced. Crevice propagation current densities were increased by one to three orders of magnitude vs. control for alloys S30400, S31603, S31725 and N08904. The effect was also reflected in greater weight loss, as well as higher maximum and average depths of attack on test alloys with biofilms on the exterior cathode surface vs. control.
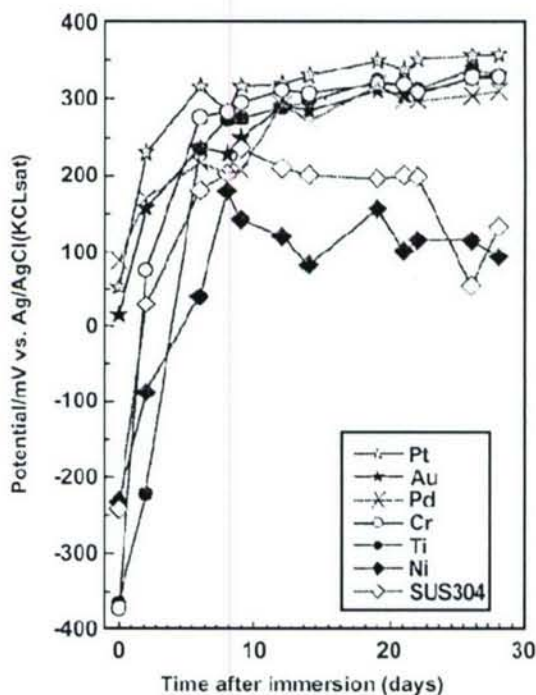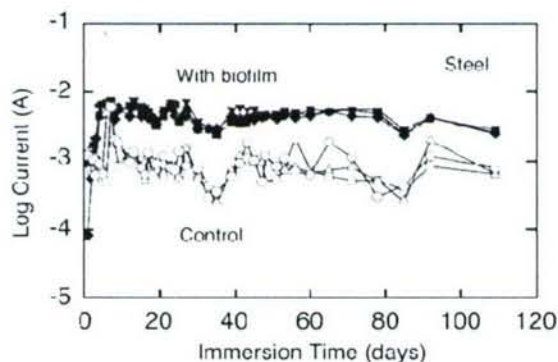
The increase in cathodic kinetics due to the action of biofilms on passive alloy surfaces also can increase the propagation rate of galvanic corrosion. Dexter and LaFontaine[14] tested galvanic corrosion of copper, 1018 carbon steel (CS), 3003 aluminum and zinc anodes coupled to cathode panels of passive alloy N08367. Natural marine microbial biofilms were allowed to form on the cathode surface. On the control tests, the action of the biofilm was prevented. Corrosion of copper, steel and aluminum anodes was significantly higher when connected to cathodes on which biofilms were allowed to grow naturally. Average corrosion currents and weight losses were 5 to 8 times higher for the steel and aluminum anodes

Figure 2. Corrosion currents for galvanic couples of UNS N08367 versus 1018 CS.[14] © NACE International 1998

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when biofilms were allowed to grow on the cathode surface than for the control without the biofilm (Figure 2).

Macrofouling organisms are found at all depths and in all seas. They are most numerous along the margins of continents where they are sometimes organized in communities of up to 500 species. A few of the larger, more prolific taxa dictate the size and shape of fouling communities, and the ability to predict fouling conditions is based on knowledge of the habits and ranges of these dominants and on their rates of colonization in various parts of the world ocean. At least 4000 different species of organisms are recorded as marine fouling nuisances. However, only the following ten groups of macrofouling organisms are usually categorized as a major nuisance: barnacles, mussels, sponges, coelenterates, bryozoans, serpulids, tunicates, amphipods, algae and marine borers.[15]

A heavy encrustation of macrofouling organisms on structural steel immersed in seawater will often decrease the corrosion rate of the steel as long as the cover of organisms remains complete and relatively uniform. The heavy fouling layer acts as a barrier, limiting dissolved oxygen at the metal surface. A layer of

Figure 3. Typical corrosion profile of steel piling in Tidal water.[20] (Reprinted with permission from Elsevier)

hard-shelled organisms, such as barnacles or mussels, on steel in the splash zone (just above the high tide level) also shields the metal from the damaging effect of wave action. Beneficial effects on general corrosion occur under uniform fouling layers. If coverage is incomplete, the fouling is more likely to cause initiation of localized corrosion by creating oxygen concentration cells. A heavy encrustation of macroorganisms also can have a number of undesirable physical effects on marine structures. The fouling layer will increase both weight and hydrodynamic drag on the structure. Interference with moving parts also may occur. A scatter of individual barnacles on a stainless steel surface will create oxygen concentration cells. The portion of the metal surface covered by the barnacle shell is shielded from dissolved oxygen in the water and thus becomes the anode. The result is crevice corrosion under the base of the barnacle. A similar effect can take place on aluminum and, to a lesser extent, on structural steel.

Accelerated low water corrosion (ALWC) or lowest astronomical tide (LAT) corrosion is a particularly aggressive form of localized corrosion that has become a high profile problem, associated with unusually high rates of metal wastage on unprotected, or inadequately protected, steel sheet pilings. Sheet piles are used as retaining walls, wharfs, and piers. In tidal waters, pilings are exposed to a range of corrosive environments, which can be classified into four zones: splash zone, tidal zone, permanent immersion, and bed zone (Figure 3). Corrosion rates in the low water level are typically 0.1 mm/year. Average corrosion rates in the range of 0.3 to 1.2 mm/side/year are typically reported for ALWC.
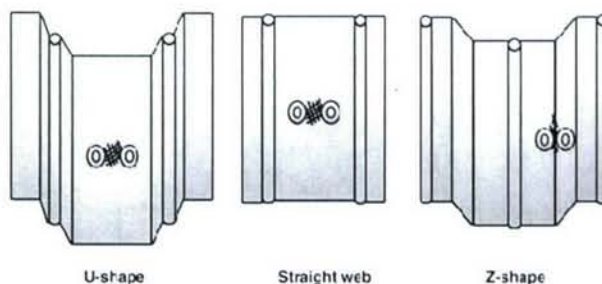
Figure 4. Location of corrosion on U-piles, straight web piles, and Z-piles.[1] © NACE International 1999
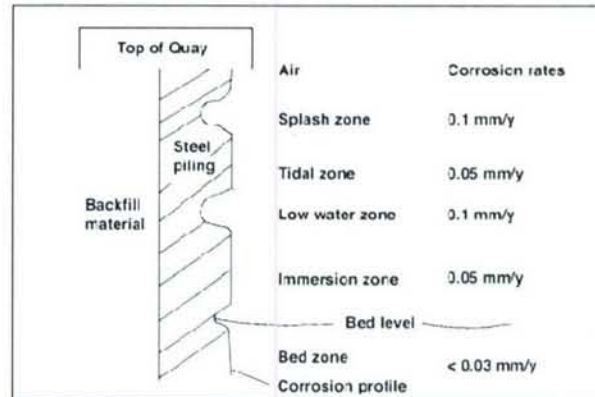
There is some question as to whether ALWC is a recent phenomenon or one that has gone unnoticed and unnamed until the 1960s. In 1914 Ellis[16] reported corrosion of steel-joist piles in Hong Kong harbor. Pits and "saucer shaped depressions" filled with black iron sulfide were found on relatively new structures at and below the low water zone, associated with corrosion rates estimated at 2 mm/side/year. Generation of hydrogen sulfide by "certain marine growths" was cited as likely being responsible.

Copenhagen[17] described a specific low water corrosion problem on steel sheet pilings at Cape Town, South Africa. Corrosion rates of 1.25 mm/side/year were

observed associated with black, sulfide rich deposits reported to be "due to the action of sulfate reducing microorganisms."

ALWC phenomenon is a global phenomenon having been reported around the world in all climatic conditions on unprotected steel pilings in contact with saline water (i.e., seawater and brackish water) that is subject to tidal influences. ALWC has been reported in the United Kingdom, Scandinavia, Belgium, Germany (Hamburg and harbors located both in the North Sea and the Baltic Sea), Holland, France, USA, Canada, South Africa, Australia, Cyprus, United Arab Emigrates, Japan, Ethiopia, and in the Southern Caribbean (Granada). A survey of port and harbor authorities in five Western European countries conducted as part of a study by the European Coal and Steel Communities concluded that at least 13 percent of the ports were affected by ALWC on steel piled structures.[18]

ALWC has a distinct appearance – patches of lightly adherent, bright orange and black (iron sulfide rich) deposits over a clean, shiny and pitted steel surface.[19-21] As the pits deepen and become more numerous, they overlap, producing a dishing effect in the metal surface, which ultimately develops into a hole. Corrosion products contain magnetite, iron sulfides, and green rust (an unstable iron oxy-hydroxide sulfate complex). ALWC also produces a specific pattern of damage on steel sheet piling. In U-shaped piles the corrosion occurs on the outpans, while in the Z-shaped sheet piles ALWC occurs in the web areas or corners (Figure 4). The pattern of damage is similar for particular pile geometries, irrespective of the geographic location of the installation.

The detailed mechanism of ALWC in marine/estuarine environments continues to be a matter of some debate but several research groups have concluded that it is a form of MIC. Gubner and Beech[1,21] conducted a statistical

A = steel pile
B = black layer
C = fouling layer
D = sea water

upper part: resembles splash zone
lower part: resembles immersion zone

(dimensions not proportional)

Figure 5. Schematic summary on the mechanism of MIC, accelerated-low-water corrosion (ALWC), on marine sheet piling structures at the low-water level.[22] © NACE International 2003

assessment of the risk of ALWC in the marine environment using a combination of biological, environmental, chemical and physical parameters. They found higher levels of total organic carbon and chloride at ALWC sites (Table 2). There were no differences in the suspended matter between the ALWC sites and sites free of the problem. They also eliminated the possibility of cyclic stress as an influence. Corrosion products were softer and easier to remove from the ALWC sites. Biofilms were present in all corrosion products, however the pH was lower beneath corrosion products at ALWC sites and the numbers of *thiobacilli* were higher.

Gehrke and Sand[22] completed a three-year study of pilings in German marine harbors with and without corrosion. They concluded that the ALWC was due to the combination of SRB and SOB (*thiobacilli*) in the fouling layers on the pilings. The organisms occurred together, separated by the oxygen gradient in the biofilm. At low tide the biofouling layer was oxygenated whereas at high tide, anaerobic areas developed. The sulfides produced by the SRB in the anaerobic regions and sulfuric acid resulting from the *thiobacilli* in the aerobic regions combined to produce an extremely corrosive environment (Figure 5).

Kumar and Stephenson[23] demonstrated that protective coatings, such as coal tar epoxy or glass flake composite can be used to mitigate ALWC. ALWC can be reduced or eliminated using sacrificial anodes in the immersed zone or impressed current cathodic protection.

Accelerated corrosion has been reported for sheet pilings in the Duluth-Superior harbor, Minnesota.[24] A diver has described the corrosion as pockmarks primarily in the four feet just below water surface. The
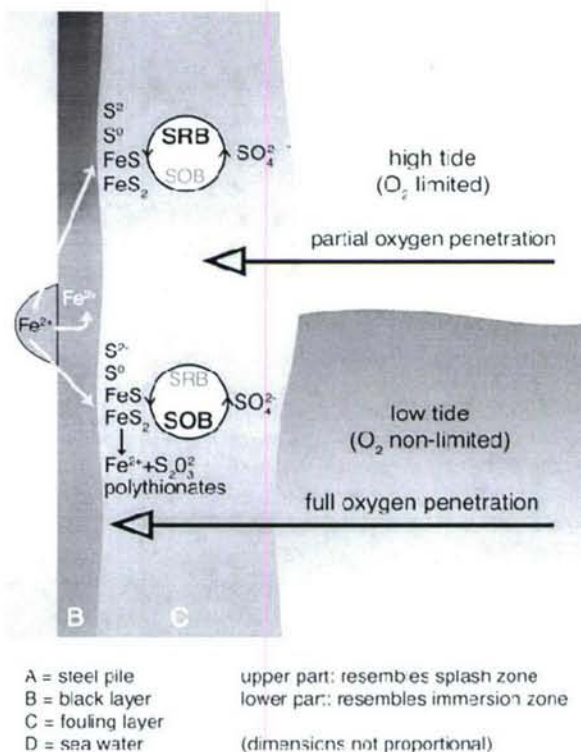
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corrosion extends down to about 10 feet, but decreases from four feet to 10 feet. Below 10 feet there is very little corrosion. Zebra mussel attachment begins at 10 feet below the surface and extends to the bottom of the sheet pile. An orange coating that tends to cover the pits covers the corroding pockmarks. The corrosion always appears upstream from the harbor. To date no mechanism for the accelerated corrosion in this fresh water harbor has been identified.

Table 2
Summary Of Statistically Significant Parameters Related To The ALWC-Corrosion Phenomenon[1]

Parameter	ALWC Mean value ± S.D.	NLWC Mean value ± S.D.	One tailed t-test
Mean tidal range (m)	3.0 ± 2.1	4.9 ± 3.0	P=0.047
- Baltic Sea data excluded (m)	3.5 ± 2.1	5.3 ± 2.9	P=0.075
Thickness of corrosion products (mm)	9.7 ± 6.4	6.1 ± 2.8	P=0.016
pH underneath corrosion products	6.2 ± 0.7	6.8 ± 0.7	P=0.021
Redox pot. of seawater ($mV_{Ag/AgCl}$)	0 ± 106	54 ± 74	P=0.05
Presence of invertebrates (%)	75%	93%	P=0.07
Presence of algae (%)	90%	67%	P=0.06
Organic carbon (%)	2.2 ± 0.5	1.4 ± 0.5	P=0.028
Organic hydrogen (%)	1.2 ± 0.2	0.8 ± 0.2	P=0.041
Organic nitrogen (%)	0.36 ± 0.06	0.31 ± 0.02	P=0.06
Total organic carbon of seawater (mg dm^{-3} O_2)	14.6 ± 13.5	7.2 ± 7.9	P=0.036
Most probable number of sulfur-oxidizing Bacteria (cells g^{-1} dry weight of corrosion products)	$6.5 \ 10^5 \pm 2.1 \ 10^6$	$3.5 \ 10^5 \pm 5.9 \ 10^5$	P=0.08

S.D. Standard deviation

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